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(54) Coloured bleaching compositions.

(57) The invention provides an aqueous, coloured bleaching composition, particularly a thickened chlorine bleaching composition, in which as colouring agent a colloiddally stable, coated pigment is used which has been coated with a bleach-resistant polymer, e.g. polystyrene. These coated pigments are colloiddally stable in the bleaching composition, in many cases more stable than uncoated pigments.

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## COLOURED BLEACHING COMPOSITIONS

The present invention relates to aqueous, coloured, bleaching compositions, particularly alkali metal hypochlorite compositions.

By bleaching compositions are meant aqueous compositions comprising an oxygen or chlorine bleaching agent, such as hydrogen peroxide, organic or inorganic persalts (with or without a bleach precursor), organic or inorganic peracids, and alkali metal hypochlorites.

Hereinafter the invention will be described and exemplified with particular reference to alkali metal hypochlorite compositions, but it is to be understood that the present invention is also applicable to the above other bleaching compositions.

Aqueous solutions of alkali metal hypochlorites have been known and used since ages unknown. Normally, they consist of an alkali metal hypochlorite, dissolved in water, and are used for general bleaching and disinfecting purposes. Such solutions are normally straw-coloured, and in order to make them more attractive and more distinguishable from other household products, attempts have been made to impart to them a more distinguishable, aesthetically attractive colour.

These hypochlorite solutions, however, form a strongly oxidizing environment, and consequently the choice of a colouring additive is very limited, restricted to only such colouring additives that are stable in these strongly oxidizing media. Potassium permanganate and potassium dichromate are such colouring agents, but they impart aesthetically less attractive colours (purple and yellow). Ultramarine Blue has also been proposed, but this pigment tends to settle out from the compositions during storage.

During the last decade, thickened aqueous hypochlorite solutions have become known and marketed. These are aqueous solutions of an alkali metal hypochlorite which have been thickened by the inclusion therein of a mixture of two different detergent surfactants. The above problems accompanying colouring aqueous hypochlorite solutions also occur on colouring such thickened compositions, but the problem of storage stability arises even with such thickened compositions. Unless major changes are made in the thickening system, the pigment particles tend to settle out, and if major changes are made, this settling out can be reduced, but the thickening effect is significantly impaired.

It has also been proposed to use a floc system in such thickened hypochlorite compositions to prevent the particulate colouring agent from settling out, such a floc system comprising, inter alia, a polymer latex. Although such a polymer latex may provide an improved physical stability of the particulate colouring agent in the hypochlorite compositions, it does not provide coloured products which are chemically stable over longer periods.

It has now been found that the chemical and physical stability of pigments as colouring agents in aqueous alkali metal hypochlorite compositions can be improved by coating the pigments with a coating of a bleach-resistant polymer.

It has already been proposed in US Patent Specifications 3,666,680 (Briggs) and 3,855,566 (Robinson) to include optical brighteners in liquid hypochlorite compositions, whereby these optical brighteners are protectively enclosed

in the inner portion of a two-layer synthetic polymer particle. This is achieved by dissolving the optical brightener in the oil-soluble monomer, copolymerizing the monomer-brightener solution with a vinyl acid, and subsequently performing a second polymerization with the hydrophobic monomer, whereby an impermeable film is formed around the previously obtained polymer-brightener particles. Although this prior proposal also mentions the possibility of using dyes and pigments such as Ultramarine Blue, Menastral Fast Green GWD, etc., it is primarily directed to optical brightening agents.

These polymer particles, however, contain a hydrophilic monomer as well, and in thickened liquid hypochlorite compositions they do not give a satisfactorily stable colour. Furthermore, these particles have an average particle size in the range of 0.1-2 micron or 0.5-2 micron, which is not suitable to produce compositions which are physically stable without the need of a suspending agent.

Recently, it has been described in GB-A1-2100307 to include a hypochlorite solution stable, suspendable dye particle in a liquid bleaching and dyeing composition. These particles contain a dye which is resistant to attack by hypochlorous acid, which dye is incorporated in a hydrophobic latex. The dye is incorporated or "embedded" in a highly hydrophobic matrix, thus shielding it from actual contact with the hypochlorite.

Dyes, however, are discrete molecular units, whereas pigments are agglomerations of molecules into particles of microscopic rather than molecular (5-50 Angstroms) dimensions. The dyes of the above proposal must be soluble in the organic/monomeric phase. In addition, low chromophore to polymer ratios are required to get a high proportion of the finished particles to be polymer to get some effective physical entrapment.

We have now found that pigments, i.e. colourants which are insoluble in the organic and aqueous phase, which have been coated with a protective coating in a single-stage process have an improved stability against attack by hypochlorite and do not cause any significant physical storage stability problems when used in an aqueous bleaching composition.

In its broadest aspect, therefore, the present invention relates to coloured aqueous alkali metal hypochlorite compositions, comprising as colouring agent a colloidal stable, coated pigment which has been coated with a bleach-resistant polymer.

Surprisingly, these coated pigments are colloidal at least as stable, or in many cases more stable than the uncoated pigments. In addition, often less coated pigment particles than dyed latices are required to colour the aqueous hypochlorite solution to the same intensity.

The invention will hereafter be described in more detail. The pigments which can be used in the present invention can be of any type, as long as they are insoluble in the organic and aqueous phase and are of a relatively small average particle size (e.g. ~ 1000 Å). They can include metallated and non-metallated synthetic pigments as well as organic and inorganic pigments.

Typical examples are given in the following list.

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Blue

<u>Pigment Name</u>	<u>C.I. N°</u>	<u>Hue</u>	<u>Type/ Structure</u>
Blue 1	42595:2	bright reddish blue	TAM/PTMA
2	44045:2	bright blue	PTMA
3	42140:1	bright blue	TPM/PTMA
4	-	bright blue	TPM/PTMA
6	-	greenish blue	TPM/PTMA
8	42140:1 + 42041:1	bright greenish blue	PTMA
9	42025:1	bright greenish blue	TPM/PTMA
12	42130	bright blue	TPM/PMA
13	-	blue	PTA
14	42600:1	bright reddish blue	TAM/PTA
18	42770:1	bright blue + bright reddish navy	TAM
19	42750:1	bright blue + bright reddish navy	TAM
20	-	bright navy	Organic pigment
21	69835	reddish navy	Anthra- quinone
23	-	blue	Organic pigment
24	42090:1	bright greenish blue	TPM
52	-	navy	Anthra- quinone
53	-	blue + greenish blue	PTMA
56	42800	greenish blue	TAM
63	73015	blue	Indigoid
66	73000	blue	Indigoid

TAM = triarylmethane

PTMA = phosphotungstomolybdic acid

TPM = triphenylmethane

60 PMA = phosphomolybdic acid

PTA = phosphotungstic acid

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Green

<u>Pigment Name</u>	<u>C.I. N°</u>	<u>Hue</u>	<u>Type/Structure</u>
Green 1	42040:1	bright bluish green	TAM/PTMA
2	42040:1 + 49005:1	bright green	TAM/PTMA
3	41000:2 + 42040:1	bright green	TAM/PTMA
4	42000	bright green	TAM
7	74260	green	Phthalo- cyanine
9	49415	green	Naphthalene sulphonic acid
11	-	green	Organic pigment
14	77199 + 77346	green	Inorganic pigment
18	-	green + bluish green	Chromium salts
47	59825	bluish green	Anthra- quinone

Other colours

<u>Pigment Name</u>	<u>C.I. N°</u>	<u>Type/Structure</u>
Red 5	12490	Monoazo
Red 48:1	15865:1	Monoazo
Red 48:2	15865:2	Monoazo
Red 48:3	15865:3	Monoazo
Red 49:1; 49:2; 49:3	15630	Monoazo
Red 52:1	15860	Monoazo
Red 53:1	15585:1	Monoazo
Red 57:1	15850:1	Monoazo
Red 81	45160:1	Xanthene/PTMA
Red 82	45150:1	Xanthene/PTMA
Red 83	58000:1	Anthraquinone
Red 90:1	45380:1	Xanthene/Al

### Other colours

<u>Pigment Name</u>	<u>C.I. N°</u>	<u>Type/Structure</u>
Violet 3	42535:1	TAM/PTMA
Violet 5:1	58055:1	Anthraquinone/Al
Violet 19	46500	Quinacridone
Yellow 14	21095	Disazo
Brown 3	21010	Disazo/DPTMA
Brown 23	-	Disazo
Brown 25	-	Monoazo
Black 3	-	Organic/PTMA
Black 5	-	Mordant/Metal

Mixtures of various pigments can equally be used. Preferably, non-metallated pigments are used in bleaching compositions which are susceptible to decomposition by metal ion catalysis, but metallated pigments when used according to the present invention show already a significant improvement in this respect in comparison with the uncoated pigments, without any significant physical stability problem. Thus it has been found that a copper-containing halogenated phthalocyanine, when used according to the present invention, causes substantially less decomposition of the bleaching composition than the same uncoated pigment, and less settling out of the pigment particles. When metallated pigments are used, it is sometimes advantageous to use a metal sequestering agent in the composition, such as a periodate or other suitable metal-chelating agent which is stable in the bleaching composition in amounts of up to about 5% by weight of the coated pigment added, to reduce the decomposition even further.

#### The Coating

The coating material to be used in the present invention should be bleach-resistant. Any organic material can be used, as long as the pigment is not soluble therein. Preferably, organic materials are used in which the pigment is readily dispersible. Suitable materials are (co)polymers prepared from a hydrophobic monomer which is capable of undergoing emulsion polymerization.

Typical examples are styrene, alkyl styrenes with one to four carbon atoms in the alkyl group, monohalogenated styrenes, acrylates, methacrylates, vinyl esters, ethylene and vinyl chloride. A particularly suitable material is polystyrene.

The coating process is carried out in a manner known per se, by introducing the pigment particles into an aqueous emulsion polymerization of styrene, using a common initiator such as potassium persulphate, azobis-(isobutyramidine hydrochloride) or 4,4'-azobis-(4-cyanovaleric acid). It has been found that higher concentrations of initiator than are usual for conventional emulsion polymerization favour the coating of the pigment particles.

The concentration ratio of monomer to pigment should be such that there is sufficient monomer present to just coat all the particles to avoid the formation of un-coloured polymeric latices. For e.g. styrene and Pigment Green 7 (C.I. N° 74260), the most effective styrene/pigment ratio was found to be 5:1.

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To aid the dispersal of the pigment in the polymerization reaction mixture, a suitable surfactant, such as a non-ionic or an anionic synthetic detergent, can be advantageously added.

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The composition

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The coated pigments of the present invention are suitable for colouring aqueous bleaching compositions, both thickened and non-thickened ones. These compositions may contain other ingredients, which are governed by the purpose for which these compositions are used, such as heavy-duty liquid fabric-bleaching and -washing compositions, liquid fabric-softening compositions, hair-bleaching compositions, hygienic cleaning compositions, hard-surface-cleaning compositions, etc. Thus, they preferably contain one or more detergent-active compounds. Further ingredients commonly encountered in such products may be included in the compositions of the invention. As said before, the bleaching agent can comprise both oxygen and chlorine bleaching agents, as well as reducing bleaches.

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The coated pigments of the present invention are particularly suitable for thickened aqueous alkali hypochlorite compositions such as described in GB-A-1329086, EP-A1-0030401, GB-A-1548379, GB-A-1466560, GB-A1-2003522, GB-A1-2041162, GB-A1-2076010 and GB-A1-2046321.

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The amount of coated pigments used in the bleach composition varies from 0.0005 to 10% by weight, preferably from 0.001 to 1% by weight.

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The invention will now further be illustrated by way of example.

In the following examples, the bleaching composition was a current commercial thickened hypochlorite bleaching composition, Domestos, manufactured and sold by Lever Brothers Ltd. This product is a product according to GB Patent 1329086.

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The colour and physical stability were assessed spectrophotometrically and visually, respectively, and the hypochlorite decomposition ("gassing") was measured by collecting the volume of gas evolved.

Example 1 - Coated Colanyl Green GG

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Pigment Encapsulation

### Pigment Encapsulation

Styrene	5.0 g
Colanyl Green GG* (Pigment Green 7 C.I. N° 74260)	2.0 g
4,4'-azobis-(4-cyanovaleric acid) (CVA)	2.0 g
Distilled water	1000 g

\* A copper phthalocyanine pigment supplied as a 50% solids aqueous paste by Hoechst (U.K.).

#### Method

Colanyl Green GG was dispersed in water (970 g) and heated to 82°C. The dispersion was purged with nitrogen for 15 minutes and styrene was added with vigorous stirring. 4,4'-azobis-(4-cyanovaleric acid) was slurried in the remaining water and added to the reactants. Polymerization was continued for 6 hours at 82°C. The latex was steam-stripped to remove any unconverted monomer and filtered through glass wool.

Transmission Electron Microscopy showed that the pigment particles were encapsulated within a sheath of polystyrene, and that the average size of these particles was 900 Å.

Styrene	5.0 g
Colanyl Green GG	2.0 g
2,2'-azobis-(2-amidino propane) HCl	2.0 g
Distilled water	1000 g

#### Method

As Example 1.

#### Stability in Thickened Hypochlorite

A sample of the above dispersion was added to Domestos at 200 ppm to give a clear, green colouration. The product retained a colour and colloidal stability for greater than 60 days.

Styrene	9.0 g
Colanyl Green GG	2.0 g
Potassium persulphate	0.5 g
Distilled water	1000 g

#### Method

As Example 1.

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#### Stability in Thickened Hypochlorite

A sample of the above dispersion was added to Domestos at 200 ppm to give a clear, green colouration. Both colour and colloidal stability were maintained for 8 weeks at 37°C. In gassing studies hypochlorite containing polymer-protected pigment showed dramatically less gassing than a sample containing Colanyl Green (order 100 times less gassing).

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#### Example 2 - Coated Colanyl Green GG

#### Pigment Encapsulation

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#### Example 3 - Coated Colanyl Green GG

#### Pigment Encapsulation

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#### Stability in Thickened Hypochlorite

A sample of the above dispersion was added to Domestos at 150 ppm to give a translucent green colouration. The product remained coloured after 60 days storage at 37°C.

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#### Example 4 - Coated Colanyl Green

## Pigment Encapsulation

Styrene	17.1 g
Colanyl Green	2.8 g
2,2'-azobis-(2-amidino propane) HCl)	0.5 g
Sodium dodecyl sulphate	1.73 g
Distilled water	250 g

## Method

15 Example 5 - Coated Pigment Blue 1

The sodium dodecyl sulphate was dissolved in the water and the encapsulation effected as in Example 1.

Pigment Encapsulation

## Stability in Thickened Hypochlorite

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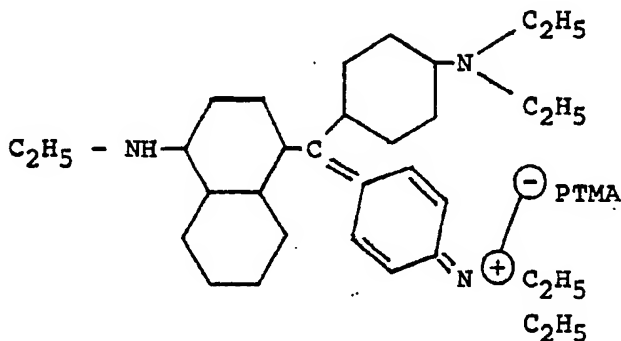
A sample of the above dispersion was added to Domestos at 150 ppm to give a translucent green colouration. The product remained coloured after 60 days storage at 25°C.

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Styrene	5.0 g
Eljon Blue Toner*	1.0 g
Arylan SNS** (20% w/w/ aqueous solution)	1.72 g
CVA	2.0 g
Distilled water	1000 g

\* Eljon Blue Toner MGS55230 obtained from Allis Jones & Co. Used as Pigment Blue 1(C.I. N° 42595:2), i.e. a phosho-tungstomolybdic acid (PTMA) salt of a triaryl-methane dye derivative:

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\*\* Arylan SNS is a naphthalene sulphonic acid formalde-hyde condensate obtained from Lankro.

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## Method

The Arylan SNS solution was mixed with the pigment and the encapsulation effected as in Example 1.

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## Stability of Thickened Hypochlorite

A sample of the above dispersion was added to Domestos at 550 ppm to give a clear blue colouration. Encapsulation enhanced the colour stability eightfold over that of the untreated pigment (120 min. vs 15 min.).

## Example 6 - Coated Pigment Violet 3



## Pigment Encapsulation

Styrene	5.0 g
Eljon Violet Toner*	1.0 g
CVA	2.0 g
Arylan SNS (20% w/w aq. solution)	1.43 g
Distilled water	1000 g

\* Eljon Violet Toner 55051 obtained from Allis Jones & Co. Used as Pigment Violet 3 (C.I. N° 42535:2), i.e. a PTMA salt of mixed methylated parosanilines.

## Method

As for Example 5.

## 15 Stability in Thickened Hypochlorite

A sample of the above dispersion was added to Domestos at 500 ppm to give a clear violet colouration. Encapsulation enhanced the colour stability threefold over that of the untreated pigment (15 min. vs 5 min.).

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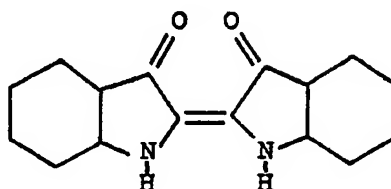
Example 7 - Coated Pigment Blue 66

## 25 Pigment Encapsulation

Styrene	5.0 g
CVA	2.0 g
Monolite Blue A-Ru*	1.0 g
Arylan SNS (20% w/w aqueous solution)	1.6 g
Distilled water	1000 g

\* Monolite Blue A-Ru obtained from ICI. Used as Pigment Blue 66 (C.I. N° 73000), i.e.:

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Example 8 - Coated Pigment Green 1

## Method

As Example 5.

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## Pigment Encapsulation

## Stability in Thickened Hypochlorite

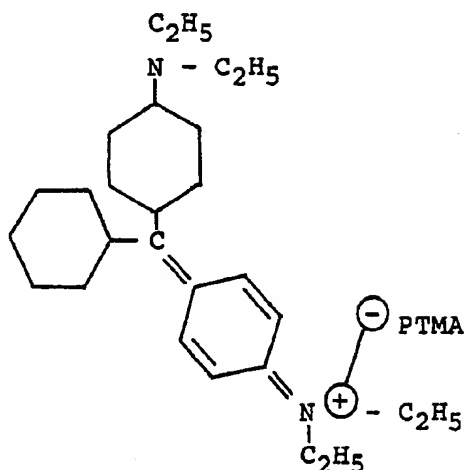
A sample of the above dispersion was added to Domestos at 500 ppm to give a blue colouration. Encapsulation enhanced the colour stability of the pigment (up to 1 hour).

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Styrene	5.0 g
Fanal Green*	1.0 g
CVA	2.0 g
Arylan SNS (20% w/w aq. solution)	1.09 g
Distilled water	1000 g

\* Fanal Green D8330 obtained from BASF. Used as  
 Pigment Green 1 (C.I. N° 42040:1), i.e. an acid salt of  
 triarylmethane dye:



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#### Stability in Thickened Hypochlorite

A sample of the above dispersion was added to  
 Domestos at 500 ppm to give a green colouration. Encap-  
 sulation enhanced the colour stability of the pigment (up to  
 20 minutes).

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#### Example 9 - Coated Pigment Blue 16

#### Pigment Encapsulation

Styrene	2.5 g
Irgazin Blue 3GT	0.4 g
CVA	1.0 g
Arylan SNS (20% w/w aq. solution)	0.7 g
Distilled water	500 g

\* Irgazin Blue 3GT supplied by Ciba Geigy. Used as  
 Pigment Blue 16 (C.I. N° 74100), i.e. unmetallated  
 phthalocyanine.

#### Method

As Example 5.

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#### Stability in Thickened Hypochlorite

A sample of the above dispersion was added to  
 Domestos at 500 ppm to give a blue colouration. Colour  
 was retained for 1 week (cf. unencapsulated pigment 3  
 days).

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#### Example 10 - Coated Pigment Brown 25

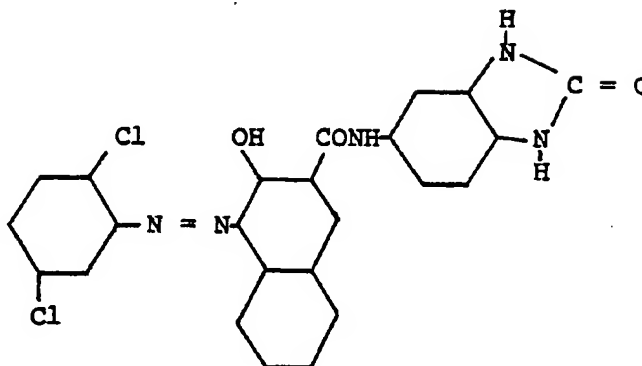
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#### Pigment Encapsulation

Styrene	5.0 g
Hostaperm Brown*	1.0 g
Arylan SNS (20% w/w aqueous solution)	1.52 g
CVA	
Distilled water	1000 g

\* Hostaperm Brown HFR supplied by Hoechst. Used as Pigment Brown 25 (C.I. N° 12510(S)), i.e. a monoazo pigment

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Method

As Example 5.

Stability in Thickened Hypochlorite

A sample of the dispersion was added to Domestos at 500 ppm to give a brown colouration. Colour was retained for 5 hours at room temperature (cf. 5 minutes for the uncoated pigment).

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Example 11 - Coated Pigment Brown 23

Pigment Encapsulation

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Styrene	5.0 g
Cromophtal Brown*	1.0 g
Arylan SNS (20% w/w aq. solution)	0.27 g
CVA	2.0 g
Distilled water	1000 g

\* Cromophtal Brown 5R supplied by Ciba Geigy. Used as Pigment Brown 23, i.e. a diazo pigment.

Method

As Example 5.

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A sample of the dispersion was added to Domestos at 500 ppm to give a brown colouration. Colour was retained for 45 minutes at room temperature.

Example 12 - Coated Remazol Green

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Pigment Encapsulation

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Styrene	8.6 g
Remazol Brilliant Green Vinyl Sulphone*	0.95 g
Sodium Dodecyl Sulphate	0.863 g
2,2'-azobis-(amidino propane) HCl	0.25 g
Distilled water	125 g

\* Remazol Brilliant Green 6B (ex Hoechst) was used as C.I. Reactive Blue 38, i.e. a phthalocyanine reactive dye.

#### Method

The vinyl sulphone derivative of Remazol Brilliant Green was generated by treating the sulphatoethyl-sulphone form of the dye with 2M aq. sodium hydroxide [e.g. see Robinson, C. *et al.*, Proc. R. Soc. (A) **31**, 576, (1931)]. The dye and surfactant were dissolved in the water, and concentrated hydrochloric acid was added until the pH of the aqueous phase was less than 1. The resulting precipitated pigment was coated as in Example 4.

#### Stability in Thickened Hypochlorite

15 A sample of the above dispersion was added to Domestos at 500 ppm to give a green colouration, which persisted for over 2 hours (cf. immediate colour loss for original dye).

20 Example 13 - Coated Remastral Blue 3G

#### Pigment Encapsulation

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Styrene	8.6 g
Remastral Blue 3G*	0.95 g
2,2'-azobis-(amidino propane) HCl	0.25 g
Sodium dodecyl sulphate	0.863 g
Distilled water	125 g

\* Remastral Blue 3G is an example of a Direct dye (ex Hoechst).

#### Method

As Example 4.

#### Stability in Thickened Hypochlorite

A sample of the above dispersion was added to Domestos at 500 ppm concentration, to give a coloured product which retained colour overnight.

#### Claims

1. An aqueous, coloured bleaching composition comprising a bleaching agent and a particulate, polymer-coated colouring agent, characterised in that the colouring agent is a

colloidally stable, coated pigment which has been coated with a bleach-resistant polymer.

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2. A composition according to claim 1, characterised in that the pigment is a metallated pigment.

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3. A composition according to claim 1 or 2, characterised in that the bleach-resistant polymer is prepared from a hydrophobic monomer.

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4. A composition according to claim 3, characterised in that the bleach-resistant polymer is polystyrene.

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5. A thickened, aqueous coloured bleaching composition, comprising a colloidally stable, coated pigment which has been coated with a bleach-resistant polymer according to any one of claims 1-4.

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